

## Acid-Enhanced Crack Initiation in Glass

T. P. DABBS AND B. R. LAWN<sup>\*,\*</sup>

Department of Applied Physics, School of Physics, University of New South Wales, Kensington,  
New South Wales 2033, Australia

*Silicate glass rods containing Vickers indentations in the subthreshold-fracture region can show dramatic strength losses on brief immersion in acid solutions. The effect is most significant for "normal" glasses, notably soda-lime glass, and for HF-based acids. After extended immersion the strength begins to recover, ultimately surpassing the original (pre-immersion) level, as glass dissolution processes become dominant. The weakening effect is interpreted in terms of chemically enhanced residual-contact stress effects.*

THE use of acid etching as a means of strengthening glass surfaces is well known. Systematic studies by Proctor<sup>1</sup> and others have demonstrated that strength increases from  $\approx 100$  MPa to  $>2$  GPa may be readily achieved by immersing glass rods in solutions of hydrofluoric acid (the most powerful of the etchants). Proctor attributed the strengthening to microcrack "blunting" resulting from dissolution of the glass at the flaw sites, an explanation generally accepted in the glass-testing field; indeed, acid-enhanced dissolution is most effectively used as a routine procedure for rendering ordinarily undetectable crack interfaces clearly visible in optical microscopy. On the other hand, Metcalfe *et al.*<sup>2,3</sup> have produced an opposite effect, i.e. a weakening, by immersing filaments of certain glass types into hydrochloric acid.

In their studies it was demonstrated that ion-exchange processes within the near-surface layers of the glass generate tensile stresses, which augment the driving forces on the flaws in subsequent strength testing. (The ion-exchange process envisaged by these workers was similar in some respects to that described by Ernsberger,<sup>4,5</sup> who used molten salts to extend, and thereby "decorate," incipient flaws in glass surfaces.) Metcalfe *et al.*<sup>2</sup> also found in the more severely treated specimens that spontaneous cracking occurred within the surface layer; the strength response of such specimens was quite distinct from that of specimens without spontaneous cracking in that the decline was considerably more marked and there was no recovery on prolonged exposure to the acid solution.

This study describes an experiment on acid-exposed indentation flaws in glass surfaces where the described strengthening and weakening characteristics are both evident. The motivation for this study came from the observation that the threshold contact load for radial crack initiation at the impression corners can, in certain glasses, be reduced substantially by briefly immersing the indented surface in dilute HF.<sup>6</sup>

A unique feature of the approach used here is the essence of control in the flaw production; the micromechanics of crack-growth to failure can, in principle, be followed at all stages of the evolution.<sup>7</sup> The indications from our observations are that the weakening effect in the present instance is controlled by the processes of crack initiation, and the strengthening effect by the processes of crack propagation (or, more strictly, inhibition of propagation).

Preliminary tests were conducted on several glasses<sup>8</sup> using different acid solutions. Indentations were made with a Vickers diamond pyramid in air and threshold loads (defined here arbitrarily as the loads at which radial cracks appeared at the impression corners 50% of the time) thereby determined. Generally, the results could be placed in two categories, according to whether the glass type was normal or anomalous in its indentation response<sup>8</sup>: with normal glasses, exposure of uncracked indentations to acid environment caused radial "pop-in" to occur after an incubation period; no such pop-in was observed with anomalous glasses. This incubation period was small,  $\approx 2$  s, for tests in a solution of 1% HF and 1% H<sub>2</sub>SO<sub>4</sub>, extending to several minutes or hours in weaker acids. (In this context it is noted that radial pop-in may occur in normal glasses upon prolonged exposure to moist air.) These results are consistent with the established existence of residual contact stresses around the indentation sites,<sup>9,10</sup> the intensity of which is substantially higher for normal than for anomalous glasses.<sup>8</sup>

Accordingly, a closer examination of the acid-enhanced pop-in phenomenon was made by conducting four-point bend tests on 5 mm diam. soda-lime glass rods which had been indented at the 50% fracture probability threshold load, 0.25 N. Soda-lime glass was chosen as representative of

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Member, the American Ceramic Society.

<sup>\*</sup>Now with the Fracture and Deformation Div., National Bureau of Standards, Washington, D. C. 20234.

the normal glasses, and the HF/H<sub>2</sub>SO<sub>4</sub> acid solution was chosen as the etchant, this combination exhibiting the effect most dramatically. The strength tests were conducted under inert conditions by thoroughly drying all specimens and operating at high-stressing rates ( $>1 \text{ GPa} \cdot \text{s}^{-1}$ ) in silicone oil, taking care to orient the rods for maximum tension at the indentation sites. Dummy runs were first made on rods which had not been subjected to the acid treatment, to establish the limits in strengths which might normally be anticipated for flaws with and without detectable radial cracking. Those specimens without cracks gave  $726 \pm 162 \text{ MPa}$  (22 tests)<sup>†</sup> (this sample excluding some rods which did not break at the indentation sites); those with cracks gave  $229 \pm 14 \text{ MPa}$  (9 tests). These two limits are indicated by shaded bands in Fig. 1. The remainder of the strength tests was run on rods initially with uncracked indentations, subjected to subsequent etch treatments for up to 20 min. The results are shown as the data points (each point representing at least 5 tests) in Fig. 1, the closed and open symbols designating the existence or otherwise of at least one radial crack segment normal to the rod axis.

Several features of interest are evident in the data trends. At etch times of  $\approx 2 \text{ s}$ , there is no indication of significant strength loss. Beyond this incubation period the strength drops abruptly, to the value observed for rods with cracks spontaneously initiated in air. The strength then remains invariant for etch times up to  $\approx 2 \text{ min}$ , after which it begins to rise. This rise continues up to and ultimately, after  $\approx 10 \text{ min}$ , surpasses the original strength for uncracked indentations.

Certain conclusions regarding mechanisms may be drawn from the behavior in Fig. 1. Beginning with the weakening stage, it is evident from the one-to-one correspondence with the pop-in event that the abrupt drop in strength must be associated with the underlying processes of crack initiation. In terms of recent microscopic studies of such processes in silicate glasses<sup>8,11-13</sup> in which it is demonstrated that intense stress concentrations can be generated at intersecting "shear bands" within the contact deformation zone, it is reasonable to suggest that initiation might be enhanced by a mechanism of preferential etching; once initiated, the cracks would be driven outward into the radial configuration by the residual stress field. In this interpretation the incubation period would correspond to the time for the active chemical species to gain access to, and interact with, the local stress concentrations. A similar explanation was proposed by Metcalfe *et al.*<sup>2,3</sup> to account for their observed weakening of glass fibers in HCl, but with the ion-exchange-generated surface tensile stresses rather than any flaw-associated residual stresses driving the freshly initiated cracks. This last point

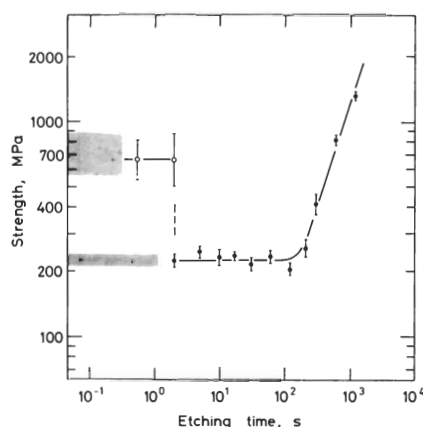


Fig. 1. Strength of Vickers-indentated (0.25 N) soda-lime glass rods as a function of immersion time in dilute HF/H<sub>2</sub>SO<sub>4</sub> solution.

is consistent with the observation by these other workers that the strength loss after incubation for specimens without spontaneously generated cracks was smooth, whereas in the present experiments the corresponding loss was abrupt; here the residual-contact field is available to operate immediately upon initiation, unlike the ion-exchange field which must build up gradually with time.

Next consider the plateau region. It might at first sight seem reasonable to expect that strengthening due to dissolution processes should begin to operate immediately after radial crack pop-in. There can be no question that access of the acid solution to the newly advanced crack tips will be effectively instantaneous, certainly relative to the 2 min period which defines the plateau in Fig. 1. That such strengthening is not immediate is attributable to the persistence of the residual-contact driving force on two aspects of the radial crack growth.

(i) *Continued, subcritical propagation.* It is well established<sup>14</sup> that acidic solutions can actually enhance crack propagation; blunting occurs only when the crack driving forces drop below some critical level, determined in the present experiment by some critical distance from the central deformation zone. (Optical examination of the cracks prior to strength testing was not sufficiently accurate to provide absolute confirmation of this predicted extension, giving  $7 \pm 1 \mu\text{m}$  and  $9 \pm 1 \mu\text{m}$  for the radial lengths at the extremes of the plateau period.)

(ii) *Strength/crack-size independence.* In the case of Vickers-indentation flaws such continued crack extension causes no further weakening. For the ultimate failure conditions in the subsequent strength test, by virtue of the crack-stabilizing effect of the residual contact term in the fracture mechanics, actually become independent of radial crack size<sup>9</sup> (with the proviso, of course, that the cracks have popped in). It may be noted that if ion-exchange stresses were to be an important factor in our experiments, the strengths of the acid-

exposed rods would be expected to decline steadily below those of the air-exposed rods in this region of behavior.

The final, strengthening stage marks the onset of crack-tip blunting. In this region the cracks show clear signs of etching. The central deformation zones also show evidence of significant attack, indicating that the residual contact stresses must be subject to removal, contributing further to strength recovery. The ultimate strength attainable after prolonged etching is limited only by glass chemistry.<sup>1</sup>

Although the present work devotes explicit attention to just one material-environment system, there are indications of some generality in the conclusions to be drawn, at least for silicate glasses which can be classified as normal. The presence of acidic solutions can promote rapid and deleterious crack initiation. Thus, measures traditionally used to strengthen surfaces may, in certain unfavorable circumstances, lead to precisely the opposite effect. The implications here are particularly pertinent to applications with ultra-high strength fibers, where the incidence of a single post-threshold flaw event could mean the loss of a component.<sup>15</sup>

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<sup>†</sup>In this work, all errors quoted are standard deviations.